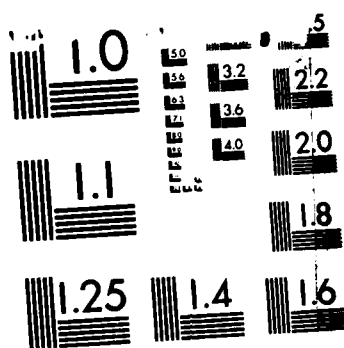


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Preparation and Characterization of
Dispersed Rh_2O_3 on Tetragonal ZrO_2

by

Y-C. Zhang, K. Dwight, A. Wold

Prepared for Publication in
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ABSTRACT

Samples of well-dispersed hexagonal Rh_2O_3 on tetragonal ZrO_2 have been prepared by the code composition of the nitrates at 900°C . A comparison of the stability towards reduction of the bulk and dispersed Rh_2O_3 products demonstrates the influence of an interaction between the dispersed metal oxide and the support.

MATERIALS INDEX: Rh_2O_3 - ZrO_2 , Catalyst-support interaction

Introduction

Recent investigations have indicated that rhodium catalysts dispersed on a number of supports have produced appreciable quantities of ethanol in the reduction of carbon monoxide with hydrogen (1-3). Somorjai (4) has reported that the formation of oxygenated products may be related to the presence of oxidized rhodium. Increased stabilization of rhodium in a higher than zero oxidation state may be achieved by possible interaction of rhodium oxide with the tetragonal zirconia support. Although oxidized rhodium may interact with the support, there is no direct evidence of a new phase being formed. Metal-support interactions have been proposed by Dall'agnol, et al. (5) to explain a much lower chemisorption of hydrogen on Rh/ZrO_2 compared to $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts. The decrease in H_2 chemisorption properties, while retaining the ability to chemisorb O_2 , has been reported to be a characteristic of Strong Metal-Support Interactions (SMSI) (6,7).

It was the purpose of this study to prepare well-dispersed samples of Rh_2O_3 on ZrO_2 and relate the structural properties of the catalysts with their stability in reducing atmospheres. Changes in the structure of the phases formed and the temperatures at which reduction to Rh metal occur could then be related to the relative strengths of the catalyst support interactions.

Experimental

Samples of dispersed Rh_2O_3 on tetragonal ZrO_2 supports were prepared to give compositions containing 5, 7.5, 10 and 15 mole percent of Rh_2O_3 . Calculated

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quantities of $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Aesar) and $\text{ZrO}(\text{NO}_3)_2$ (9) were dissolved in water. Ten ml of water was added for each gram of total nitrates. For example, 160 mg $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and 1.058g $\text{ZrO}(\text{NO}_3)_2$ were dissolved in 12 ml of water to give a 5 mole percent loading of Rh_2O_3 in the final product. The molecular weights of $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2$ were determined by thermogravimetric analysis as 320 and 235 respectively compared to the calculated values of 325 and 231. The solution was then dried at 150°C for 12 hours, ground, and ignited at 400°C for 24 hours. The sample was then ground and heated in air to 900°C .

Temperature programmed decomposition of both rhodium nitrate and the double salt of rhodium nitrate and zirconyl nitrate were carried out in a Cahn System 113 thermal balance. Both bulk rhodium nitrate and 30 mole percent rhodium nitrate-70 mole percent zirconyl nitrate were dissolved in water and then dried at 150°C in air for 12 hours. The partially decomposed products were then decomposed in the balance under a predried oxygen atmosphere at a flow rate of 60 cc/min. The samples were heated to 950°C at a rate of 100°C/hr .

The temperature programmed reductions of both bulk Rh_2O_3 and 15 mole percent Rh_2O_3 on ZrO_2 were carried out using the same balance. A concentration of 15 mole percent rhodium oxide loading was chosen because at this concentration changes in the phases produced on reduction could readily be resolved by x-ray diffraction. Before the reduction was started, it was necessary to preheat the sample in dry oxygen up to 900°C in order to remove any adsorbed water. After the sample was allowed to cool to room temperature, a 85/15 mixture of Ar/H_2 was predried and passed at a rate of 60 ml/min into the TGA balance. The temperature was then increased to 500°C at a rate of 50°C/hr .

Characterization of Products

X-ray powder diffraction patterns of the samples were obtained using a Phillips diffractometer and monochromated high intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405\text{\AA}$). The diffraction patterns were taken in the range $12^\circ < 2\theta < 80^\circ$ with a scan rate of $1^\circ 2\theta \text{ min}^{-1}$ and a chart speed of 30 in h^{-1} .

The surface areas were measured by the BET method using a Flow Sorb (II) 2300 (Micromeritics Instrument Corp., Norcross, GA). The samples were degassed at 250°C for 30 minutes and the adsorbate gas consisted of a mixture of 30% N_2 and 70% He.

Results and Discussion

Samples of Rh_2O_3 dispersed on ZrO_2 were prepared by double decomposition of $\text{ZrO}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$. The temperature programmed decomposition of both bulk rhodium nitrate and bulk zirconyl nitrate, as well as the double salt of rhodium and zirconyl nitrates were carried out in order to compare their decomposition temperatures. Pure rhodium nitrate decomposes to the sesquioxide at approximately 560°C . The final product gave an x-ray pattern which corresponded to that of hexagonal Rh_2O_3 . These results are in agreement with those reported by Bayer and Wiedemann (10). Decomposition of zirconyl nitrate proceeds completely below 500°C and the final product is tetragonal ZrO_2 . However, the final stage of weight loss for the double nitrates occurred at a

higher temperature, between 780°C and 900°C. X-ray analysis of the final product identified the phases as hexagonal Rh_2O_3 and tetragonal ZrO_2 . Hence, in order to be certain that the final product contains only Rh_2O_3 and ZrO_2 the nitrates must be decomposed at a temperature of 900°C.

X-ray patterns of the phases produced by the decomposition of the nitrates for 24 h in air at 900°C indicated that even at this temperature the tetragonal ZrO_2 phase was poorly crystallized. The peaks are broad, so that the splitting of the (020), (002); (220), (022); (131), (113) are barely discernable. Decomposition of pure zirconyl nitrate in the absence of Rh occurs below 500°C and the tetragonal splittings of the same reflections are relatively sharp. Furthermore, the stability of the tetragonal ZrO_2 in the presence of Rh_2O_3 persists beyond 900°C, whereas in the absence of Rh_2O_3 , the tetragonal phase begins to transform to monoclinic ZrO_2 at 600°C, and at 800°C 90% of the product is the monoclinic phase (8). A loading of 15 mole percent rhodium oxide heated to 900°C appears in the x-ray diffraction patterns as the poorly crystallized hexagonal phase. X-ray diffraction patterns of products containing less than 10 mole percent Rh_2O_3 heated to this temperature indicate the phase is amorphous. Fig. 1 compares the x-ray diffraction results of a dispersed Rh_2O_3 on ZrO_2 at a 7.5 mole percent loading compared to an equivalent mechanical mixture of two well-crystallized phases.

Comparison of the surface areas of pure ZrO_2 and Rh_2O_3 with various loadings of dispersed Rh_2O_3 and ZrO_2 are given in Table 1. The surface areas for both bulk materials were low, but as soon as even 5 mole percent of Rh_2O_3 was dispersed on ZrO_2 , the surface area greatly increased. At concentrations of Rh_2O_3 greater than 10 mole percent, there was no further increase in the surface area. This was consistent with the first appearance of detectable Rh_2O_3 in the x-ray diffraction patterns of the products.

TABLE I

Composition ^a	Surface Area (m^2/g)	Phases
ZrO_2	2.3	mono and tet ZrO_2
$\text{Rh}_2\text{O}_3/\text{ZrO}_2$ (5%)	33.0	tet ZrO_2
$\text{Rh}_2\text{O}_3/\text{ZrO}_2$ (7.5%)	37.6	tet ZrO_2
$\text{Rh}_2\text{O}_3/\text{ZrO}_2$ (10%)	38.5	tet ZrO_2 and hex Rh_2O_3
$\text{Rh}_2\text{O}_3/\text{ZrO}_2$ (15%)	35.9	tet ZrO_2 and hex Rh_2O_3
Rh_2O_3	2.7	hex Rh_2O_3

^aSamples prepared from decomposition of nitrates at 900°C.

The temperature programmed reduction studies on both bulk Rh_2O_3 and 15 mole percent Rh_2O_3 dispersed on ZrO_2 are shown in Fig. 2. Tetragonal ZrO_2 does not lose any weight during the reduction process and hence the ZrO_2 weight can be

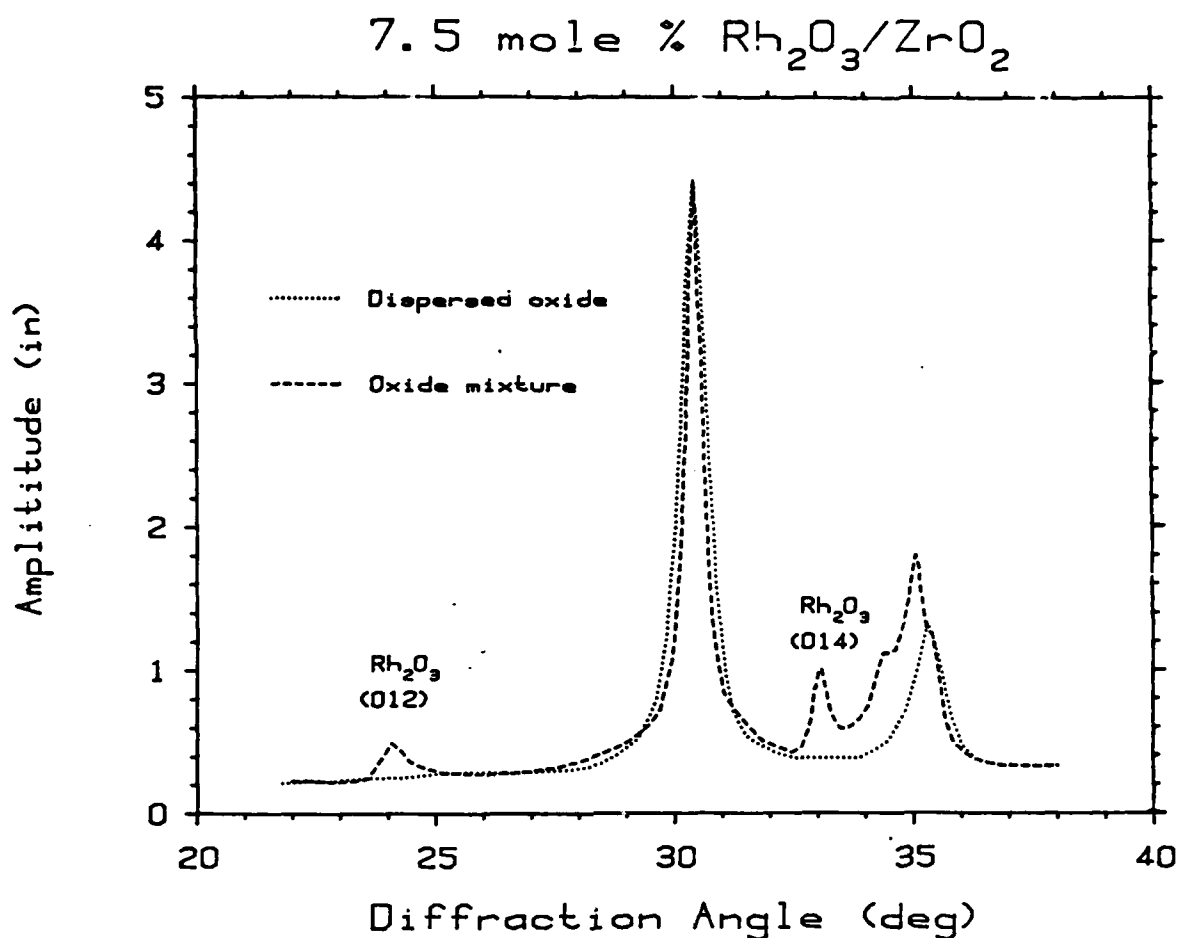


Fig.1

Comparison between the x-ray patterns of two samples containing 7.5 mole percent Rh_2O_3 on ZrO_2 . The characteristic peaks of hexagonal Rh_2O_3 are evident for the mechanical mixture, but are absent in the case of the dispersed oxide prepared from decomposition of the mixed nitrates.

subtracted from the total weight of the dispersed sample. Bulk Rh_2O_3 is completely reduced to Rh metal at 125°C , whereas the reduction of the dispersed sample was not complete until 180°C . This increase in the reduction temperature of dispersed hexagonal Rh_2O_3 is consistent with the existence of an interaction between the hexagonal Rh_2O_3 and the tetragonal ZrO_2 support. After reduction of the dispersed oxides at 200°C , in the presence of Rh metal, tetragonal ZrO_2 was poorly crystallized. Upon heating to 850°C it remained a tetragonal phase but at this temperature the characteristic tetragonal splitting was pronounced. At 900°C , tetragonal ZrO_2 begins to convert to the monoclinic phase. This is in contrast to pure tetragonal ZrO_2 (no metallic Rh) which remains tetragonal only to 600°C . This increased stabilization of the tetragonal phase in the presence of Rh metal may also be related to a metal-support interaction.

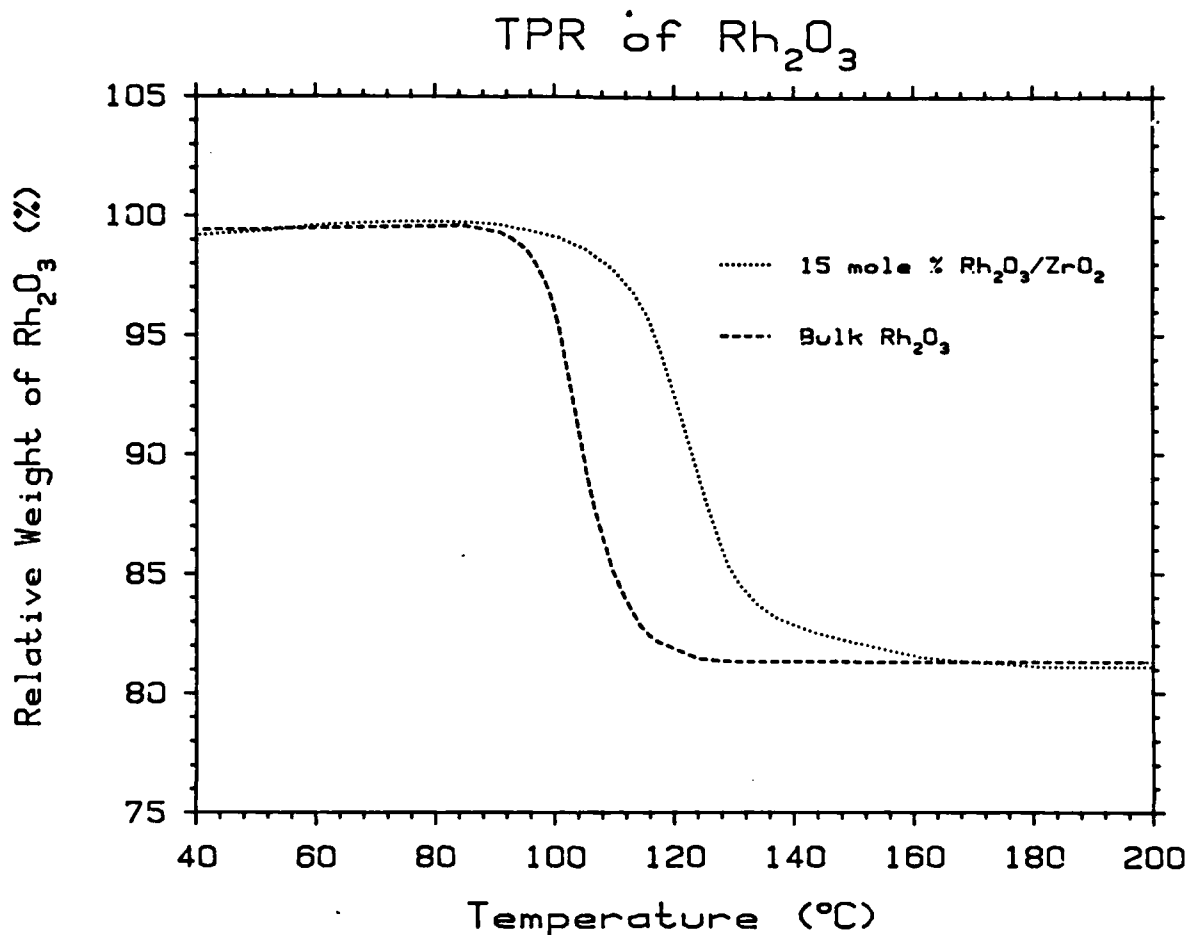


Fig.2

Temperature programmed reduction of bulk Rh_2O_3 in 85/15 Ar/ H_2 compared with that of 15 mole percent Rh_2O_3 dispersed on ZrO_2 . The variations with temperature of the relative weight per Rh_2O_3 (exclusive of ZrO_2) for these two samples demonstrate that the dispersed oxide is more stable towards reduction.

Acknowledgments

This research was supported in part by the Office of Naval Research and Eastman Kodak Company, Rochester, NY. The authors also wish to acknowledge the support of the National Science Foundation for the partial support of K. Dwight and the use of the Materials Research laboratory at Brown University which is funded by the National Science Foundation.

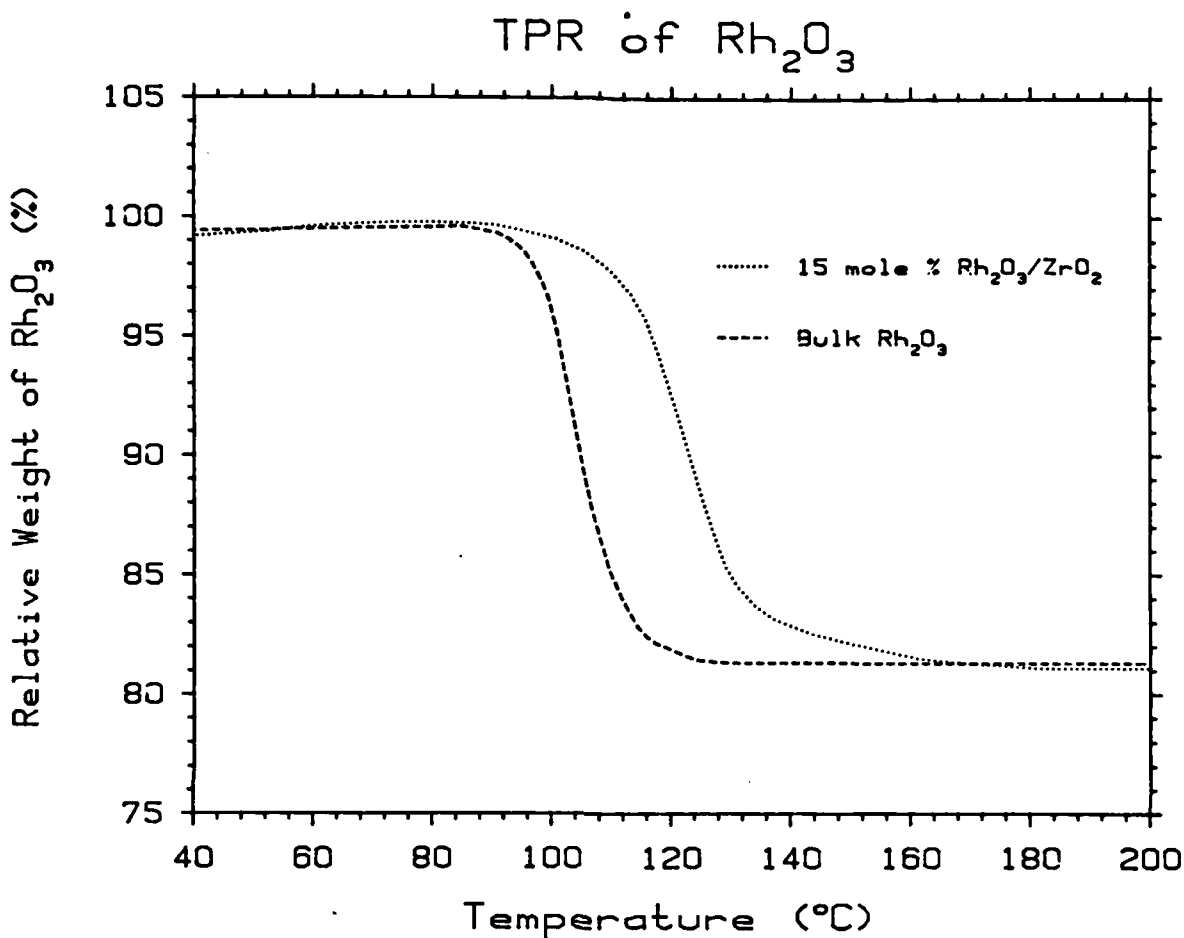


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